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13. ABSTRACT (Maximum 200 words) This project has covered a number of areas related to theoretically modelling FEL laser interactions with materials. In particular we have been interested in developing models for incorporation or the essential aspects of the laser interactions into a molecular dynamics (MD) model as the MD approach provides a microscopic picture of atomic motions.				
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This project has covered a number of areas related to theoretically modeling FEL laser interactions with materials. In particular we have been interested in developing models for incorporation of the essential aspects of the laser interaction into a molecular dynamics (MD) model as the MD approach provides a microscopic picture of atomic motions. Since this project has spanned seven years, we will concentrate on the most recent work in this report.

The highlight of our accomplishments is the recent development of a breathing sphere model for laser ablation of solids. The essence of this model is to treat each molecule (rather than an atom) as the particle of interest in the simulation. In addition to the traditional translational degrees of freedom, though, the molecules can breathe or change size. This allows us to incorporate realistic rates of energy transfer from individual molecules to the surrounding material. Specific properties of the laser such as pulse width, wavelength, fluence can be incorporated. In addition, heterogeneous samples can be modeled. The highlights to date are given below.

- The microscopic mechanisms of laser ablation are delineated. The laser induced pressure buildup and the phase explosion due to overheating of the irradiated material are identified as the key processes that determine the dynamics of laser ablation.
- The fluence threshold behavior in laser ablation is predicted. The physics of the material removal below and above threshold is analyzed.
- An expression for the analytical description of the velocity distribution in laser ablation is proposed based on the simulation results.
- Conditions for desorption of large analyte molecules in matrix assisted laser desorption (MALDI) are studied. The existence of the fluence threshold for the ejection of analytes, high kinetic energies and weak mass dependence of the ejection velocities on the molecular mass as well as the conditions that provide survivability of large fragile biomolecules in MALDI are addressed.
- Photomechanical the thermal damage mechanisms within adsorbing granules embedded into a transparent medium are studied and related to the experimental observations for pigmented tissues. A strong pulse width dependence of the threshold energy for producing a visible damage to the absorbing granule and the mechanism of the damage is observed. The acoustic impedance mismatch at the interface between the absorbing granule and the surrounding medium is found to define the role of the intragranular fracturing in short pulse laser damage.

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Publications:

Molecular Dynamics Simulations of Growth and Etching Reactions on Silicon Surfaces, D. Srivastava, T. A. Schoolcraft and B. J. Garrison, in *Process Physics and Modeling in Semiconductor Technology*, ed. J. D. Plummer, S. T. Pantelides and G. R. Srinivasan, Vol. 91, 3 (1991).

Angular Distributions of Rh Atoms Desorbed from Ion-Bombarded Rh{100}: Effect of Local Environment, R. Maboudian, Z. Postawa, M. El-Maazawi, B. J. Garrison and N. Winograd, *Phys. Rev.* **B42**, 7311-7316 (1990).

Modeling the Growth of Semiconductor Epitaxial Films via Nanosecond Time-scale Molecular Dynamics Simulations, D. Srivastava, B. J. Garrison and D. W. Brenner, *Langmuir* **7**, 683-692 (1991).

The Dynamics of Surface Rearrangements in Si Adatom Diffusion on the Si{100}-(2x1) Surface, D. Srivastava and B. J. Garrison, *J. Chem. Phys.* **95**, 6885-6891 (1991).

Quantification of the Strain in Fully Relaxed Si/Ge Heteroepitaxial Films and Superlattices via Molecular Dynamics, D. Srivastava, R. S. Taylor and B. J. Garrison, *J. Vac. Sci. Technol.* **B9**, 1517-1523 (1991).

The Initial Stages of Etching of the Si{100}(2x1) Surface by 3.0 eV Normal Incident Fluorine Atoms: A Molecular Dynamics Study, T. A. Schoolcraft and B. J. Garrison, *J. Am. Chem. Soc.* **113**, 8221-8228 (1991).

Energy- and Angle-Resolved Measurements of the Rh(⁴F_{9/2}) and Rh(⁴F_{7/2}) Populations from Ion Bombarded Rh{100}, N. Winograd, M. El-Maazawi, R. Maboudian, Z. Postawa, D. N. Bernardo and B. J. Garrison, *J. Chem. Phys.* **96**, 6314-6317 (1992). Erratum: *ibid* **100**, 8557 (1994).

The Angular Distribution of Ga⁺ Ions Desorbed by 3 keV Ion Bombardment of GaAs{001} (2x4), R. Blumenthal, K. P. Caffey, E. Furman, B. J. Garrison and N. Winograd, *Phys. Rev.* **B44**, 12830-12836 (1991).

Surface Characterization and Adsorbate-Site Determination Using Multiphoton Resonance Ionization Detection of Desorbed Particles, M. El-Maazawi, Z. Postawa, R. Maboudian, B. J. Garrison and N. Winograd, 5th International Symposium on Resonance Ionization Spectrometry and Its Applications (RIS 90), *Inst. Phys. Conf. Ser. No.* **114**, 451-454 (1991).

Molecular-Dynamics Simulations of Dimer Opening on a Diamond {001}(2x1) Surface, B. J. Garrison, E. J. Dawnkaski, D. Srivastava, and D. W. Brenner, *Science* **255**, 835-838 (1992).

Ion Pick-up of Large, Surface-Adsorbed Molecules: A Demonstration of the Eley-Rideal Mechanism, E. R. Williams, G. C. Jones, Jr., L. Fang, R. N. Zare, B. J. Garrison, and D. W. Brenner, *J. Am. Chem. Soc.* **114**, 3207-3210 (1992).

Angle-Resolved Velocity Distributions of Excited Rh Atoms Ejected from Ion-Bombarded Rh{100}, D. N. Bernardo, M. El-Maazawi, R. Maboudian, Z. Postawa, N. Winograd and B. J. Garrison, *J. Chem. Phys.* **97**, 3846-3854 (1992). Erratum: *ibid* **100**, 8557 (1994).

GaAs{001}(2x4) Surface Structure Studies with Shadow-Cone-Enhanced Secondary Ion Mass Spectrometry, C. Xu, K. P. Caffey, J. S. Burnham, S. H. Goss, B. J. Garrison and N. Winograd, *Phys. Rev.* **B45**, 6776-6784 (1992).

Angular Distribution of Ga⁺ Ions Desorbed by 3 keV Ion Bombardment of GaAs{001} (2x4), B. J.

Garrison, R. Blumenthal, K. Caffey, E. Furman and N. Winograd, Secondary Mass Spectrometry, SIMS VIII, eds. A. Benninghoven, K. T. F. Janssen, J. Tümpner, and H. W. Werner, (John Wiley & Sons, Chichester, 1992), 65-68.

Molecular Dynamics Simulations of Surface Chemical Reactions, B. J. Garrison, Chem. Soc. Reviews, Vol. 21, 155-162 (1992).

The Adsorption and Diffusion Dynamics of a Ge Adatom on the Si{100} (2x1) Surface, D. Srivastava and B. J. Garrison, Phys. Rev. **B46**, 1472-1479 (1992).

Unimolecular Decomposition in the Sputtering of Metal Clusters, A. Wucher and B. J. Garrison, Phys. Rev. **B46**, 4855-4864 (1992).

Combining Molecular Dynamics and Monte Carlo Simulations to Model Chemical Vapor Depositions: Application to Diamond, D. W. Brenner, D. H. Robertson, R. J. Carty, D. Srivastava and B. J. Garrison, Materials Research Soc. Meeting Symposium Proceedings, **278**, 255 (1992).

Production of Excited Rh Atoms via keV Particle Bombardment of Rh{100}: Simulation of Excitations due to Collisions Above the Surface, D. N. Bernardo and B. J. Garrison, J. Chem. Phys. **97**, 6910-6916 (1992).

Ion Beams and Lasers - New Directions for Surface Analysis, B. J. Garrison and N. Winograd, Chemtech, January, 25-31 (1993).

Molecular Dynamics Investigation of the MBE Growth of Si on Si{110}, M. F. Crowley, D. Srivastava and B. J. Garrison, Surf. Sci. **284**, 91-102 (1993).

The Si Adatom Dynamics and Mechanisms of the Epitaxial Growth on a Single-Height Stepped Si{001} Surface, D. Srivastava and B. J. Garrison, Phys. Rev. **B47**, 4464-4474. (1993).

keV Particle Bombardment of Solids: Molecular Dynamics Simulations and Beyond, D. N. Bernardo, R. Bhatia and B. J. Garrison, Comp. Phys. Comm., **80**, 259-273 (1994).

The Simulation of Energetic Particle Collisions with Solids - a Visual Representation, R. Webb, R. Smith, E. Dawnkaski, B. Garrison and N. Winograd, International Video J. of Engineering Research (Gordon & Breech) **3**, 63-72 (1993).

Hydrogen Abstraction Reactions in the keV Particle Bombardment of Organic Films, R. S. Taylor and B. J. Garrison, J. Am. Chem. Soc., **116**, 4465-4466 (1994).

Mechanistic Analysis from Molecular Dynamics Simulations: keV Particle Induced Desorption from Si{001}, D. E. Sanders, K. B. S. Prasad, J. S. Burnham and B. J. Garrison, Phys. Rev. **B50**, 5358-5369 (1994).

Time-Dependent Monte Carlo Simulations of Radical Densities and Distributions on the Diamond{001}(2x1):H Surface, E. J. Dawnkaski, D. Srivastava and B. J. Garrison, Chem. Phys. Lett. **232**, 524-530 (1995).

Energy-Resolved Angular Distributions and the Population Partition of Excited State Rh Atoms Ejected From Ion Bombarded Rh{001}, C. He, Z. Postawa, M. El-Maazawi, S. Rosencrance, B. J. Garrison and N. Winograd, J. Chem. Phys. **101**, 6226-6232 (1994).

Submonolayer Structure of An Abrupt Al/GaAs{001}-(2x4) Interface, J. S. Burnham, D. E. Sanders, C. Xu, R. M. Braun, S. H. Goss, K. P. Caffey, B. J. Garrison and N. Winograd, Phys. Rev. **B53**, 9901-9906 (1996).

Molecular Desorption in Bombardment Mass Spectrometries, R. S. Taylor, C. L. Brummel, N. Winograd, B. J. Garrison, J. C. Vickerman, Chem. Phys. Lett. **233**, 575-579 (1995).

Molecular Dynamics Simulations of Fluorine Molecules Interacting with a Si{100}(2x1) Surface at 1000 K, T. A. Schoolcraft, A. M. Diehl, A. B. Steel and B. J. Garrison, J. Vac. Sci. Technol. **A13**, 1861-1866 (1995).

Time Dependent Monte Carlo Simulations of H Reactions on the Diamond{001}(2x1) Surface Under Chemical Vapor Deposition Conditions, E. J. Dawnkaski, D. Srivastava and B. J. Garrison, J. Chem. Phys. **102**, 9401-9411 (1995).

Potential Energy Surfaces for Chemical Reactions at Solid Surfaces, B. J. Garrison and D. Srivastava, Ann. Rev. Phys. Chem. **46**, 373-394 (1995).

A Mechanistic Study of Atomic Desorption Resulting from the keV Ion Bombardment of fcc{001} Single Crystal Metals, S. W. Rosencrance, J. S. Burnham, D. E. Sanders, C. He, B. J. Garrison, N. Winograd, Z. Postawa and A. E. DePristo, Phys. Rev. **B52**, 6006-6014 (1995).

Band Structure Effects in Ejection of Ni Atoms in Fine Structure States, C. He, Z. Postawa, S. W. Rosencrance, R. Chatterjee, B. J. Garrison and N. Winograd, Phys. Rev. Lett. **75**, 3950-3953 (1995).

Angular, Energy and Population Distributions of Neutral Atoms Desorbed by KeV Ion Beam Bombardment of Ni{100}, C. He, S. Rosencrance, Z. Postawa, C. Xu, R. Chatterjee, D. E. Reiderer, B. J. Garrison and N. Winograd, Nucl. Inst. and Meth. B **100**, 209-212 (1995).

Ion-Induced Emission of Excited Atoms from (100) Surfaces of Transition Metal Single Crystals, Z. Postawa, C. He, M. El-Maazawi, R. Chatterjee, B. J. Garrison, S. W. Rosencrance and N. Winograd, Vacuum **46**(5/6), 605-608, (1995).

Desorption Mechanism of Benzene from C₆H₆/Ag(111) Using keV Ion Bombardment and Laser Postionization, R. Chatterjee, D. E. Riederer, B. J. Garrison and N. Winograd, Resonance Ionization Spectroscopy 1996, Institute of Physics Conference Series Number 388, 375-378 (1996).

Modeling of Surface Processes as Exemplified by Hydrocarbon Reactions, B. J. Garrison, P. B. S. Kodali and D. Srivastava, Chemical Reviews **96**, 1327-1341 (1996).

Temperature Dependence of Polar Angle Distributions of Atoms Ejected from Ion Bombarded Au{111}, S. W. Rosencrance, N. Winograd, B. J. Garrison and Z. Postawa, Phys. Rev. **B53**, 2378-2384 (1996).

Growth of Diamond Films on a Diamond{001}(2x1):H Surface by Time Dependent Monte Carlo Simulations, E. J. Dawnkaski, D. Srivastava and B. J. Garrison, J. Chem. Phys. **104**, 5997-6008 (1996).

Intermediate Metastable Structure of the C{111}/(1x1)H-C{111}/(2x1) Surface Phase Transition, L. V. Zhigilei, D. Srivastava and B. J. Garrison, Phys. Rev. B **55**, 1838-1843 (1997).

Vibrational Dynamics of the CH Stretching Mode of H-Terminated Diamond Surfaces, L. V. Zhigilei, D. Srivastava and B. J. Garrison, Surf. Sci., **374**, 333-344 (1997).

Pushing the Limits of Classical Modeling of Bombardment Events in Solids, R. Chatterjee and B. J. Garrison, Radiation Effects and Defects in Solids, Radiation Effects and Defects in Solids, **142**, 127-145 (1997).

Molecular Dynamics Model for Laser Ablation of Organic Solids, L. V. Zhigilei, P. B. S. Kodali and B. J. Garrison, J. Phys. Chem. B **101**, 2028-2037 (1997).

Angle-Resolved SIMS Studies of $\text{Al}_x\text{Ga}_{(1-x)}\text{As}$ {001} (2x4) Surface Reconstruction, S. H. Goss, P. B. S. Kodali, B. J. Garrison and N. Winograd, *Surf. Sci.*, **387**, 44-49 (1997).

On the Threshold Behavior in the Laser Ablation of Organic Solids, L. V. Zhigilei, P. B. S. Kodali and B. J. Garrison, *Chem. Phys. Lett.*, **276**, 269-273 (1997).

Velocity Distributions of Molecules Ejected in Laser Ablation, L. Zhigilei and B. J. Garrison, *Appl. Phys. Lett.* **71**(4) 551-553 (1997).

Molecular Dynamics Simulations of Reactions Between Molecules: High Energy Particle Bombardment of Organic Films, B. J. Garrison and R. S. Taylor, *Secondary Ion Mass Spectrometry, SIMS X*, (John Wiley & Sons, 1997), 951-964.

Computer Simulation Study of Damage and Ablation of Submicron Particles from Short Pulse Laser Irradiation, L. V. Zhigilei and B. J. Garrison, *Appl. Surf. Sci.*, in press (1998).

A Microscopic View of Laser Ablation, L. V. Zhigilei, P. B. S. Kodali and B. J. Garrison, *J. Phys. Chem.*, submitted (1998).

Phase Transition at Low Fluences in Laser Desorption of Organic Solids: A Molecular Dynamics Study, P. B. S. Kodali, L. V. Zhigilei and B. J. Garrison, *J. Chem. Phys.*, submitted (1998).